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[74] Patent agency: China Petroleum & Chemical Co, Lanzhou Chemical Industry Co. Patent Agency

[71] Patentee: Lanzhou Chemical Industry Co.
Research Institute of Chemical
Industry
Address: Heshui Rd. 1#, Xi Gu District,
Lanzhou, Gansu Province
730060

Agent: YANG, Guang;
WANG, Jianming

[72] Inventor(s):GUO, Changrong;
LIU, Hao;
WANG, Xingya;
ZHU, Jingfang;
ZHOU, Zhiping;

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10 [54] Title of the patent: Preparation method of styrene-butadiene block copolymer
[57] Abstract

15 The present invention relates to a process for producing styrene-butadiene random block copolymer. Random block is generated after non-elastic block is formed during anionic polymerization of styrene-butadiene that is initiated by organolithium and elastic structural-regulated block is finally formed. By use of lithium-base polymer chain with active end, which is created by coupling of alkoxysilicon compound, at this time, a styrene-butadiene random block copolymer with star structure is generated.

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Claims

1. A process for producing styrene-butadiene block copolymer using tri-alkoxysilicon compound as coupling reagent, or producing random block copolymer of formula $(S-S_1-B/S_2-B_1)_m-X-(B_1-B_2/S-S_1)_n$ using polycyclic oxide (such as epoxidized polybutadiene, epoxidized soybean oil, epoxidized flaxseed oil), polyester (such as adipate), halide (such as silicon tetrachloride), polyisocyanate (such as benzene-1,2,4-triisocyanate), polyamine, polyketone, polybase, and anhydride (such as pyromellitic anhydride) as coupling reagent; which characterized in that the styrene-butadiene random block copolymer with star structure is generated by using tri-alkoxysilicon compound as coupling reagent.
5
2. The process of claim 1, which characterized in that said random block copolymer with star structure can be represented by formula $(S-B'/S-B')_n-X$, wherein S represents polyethylene aromatic hydrocarbon block, B' represents conjugated diene block, B'/S represents random copolymer block of monovinyl aromatic hydrocarbon and conjugated diene, n is an integer between 3~4, X represents residue of coupling reagent.
10
3. The process of claim 1, which characterized in that the monovinyl aromatic hydrocarbon is styrene, the conjugated diene is 1,3-butadiene, and the initiator is s-butyl lithium.
15
4. The process of claim 1, which characterized in that the structure of said tri-alkoxysilicon compound is $R-Si(OMe)_3$, wherein R is C_1-C_{12} straight chain alkyl, cycloalkyl and aryl.
20

Specification

Preparation method of styrene-butadiene block copolymer

The present invention relates to a process for producing styrene-butadiene block copolymer, which comprises using tri-alkoxysilicon compound $RSi(OR)_3$ as coupling reagent to couple active polymers containing random blocks.

There are many methods reported in the prior art for producing styrene-butadiene block copolymer. As described in US Patent No. 3880954, after polymerization of styrene and butadiene successively, active chains of styrene and butadiene blocks are coupled by methyl trimethoxy silicane to 10 prepare copolymer; Another copolymer as disclosed in Japan Application Laid-Open Sho 63-92629 is expressed by formula $(S-S_1-B/S_2-B_1)_m-X-(B_1-B_2/S-S_1)_n$, wherein X is multifunctional group, m and n are integers equal to the functionality of X, and their values are between 3 and 20 (m≤n), S and S_1 represent copolymer blocks of vinyl aromatic hydrocarbon 15 monomer, B_1 represents conjugated diene elastic block which present in an amount of no more than 20% of the copolymer, B/S_2 and B_2/S represent random blocks of vinyl aromatic hydrocarbon and conjugated diene, or blocks with degressive vinyl aromatic hydrocarbon in copolymer of vinyl aromatic hydrocarbon and conjugated diene. In this method, polycyclic oxide (such as 20 epoxidized polybutadiene, epoxidized soybean oil, epoxidized flaxseed oil), polyester (such as adipate), halide (such as silicon tetrachloride), polyisocyanate (such as benzene-1,2,4-triisocyanate), polyamine, polyketone, polybase, and anhydride (such as pyromellitic anhydride) are used as coupling reagent.

The impact strength of block copolymers produced by the above methods is 25 not satisfying. When elevating the impact strength, the overall performances are significantly declined.

The object of the present invention is to provide a process for producing styrene-butadiene random block copolymer using tri-alkoxysilicon compound as coupling reagent, so as to improve the impact strength and transparency of 30 resin.

To achieve the above object, the present invention provides a block copolymer of formula $(S-B/S'-B')_n-X$, wherein S represents polyethylene aromatic hydrocarbon block, B/S' represents random copolymer block of vinyl aromatic hydrocarbon and conjugated diene, B' represents conjugated diene block, n is an integer between 3~4, X represents residue of coupling reagent.

In the process of the invention, non-elastic (resinic) chain block is produced

firstly. And 70~95% of vinyl aromatic hydrocarbon is added into a polymerization kettle, after contacting with organolithium initiator and stirring for 20~60 minutes, the vinyl aromatic hydrocarbon is transformed into a non-elastic chain block with an active lithium atom end. Thereafter, the residual mixture of monovinyl aromatic hydrocarbon and conjugated diene is added into the kettle, wherein the conjugated diene presents in an amount of 80~99%. After reacting for 5~120 minutes at 0~110℃, random copolymer block of monovinyl aromatic hydrocarbon and conjugated diene is formed. The monomer mixture can be added into the reaction kettle successively (feeding speed should be lower than reaction speed); random reagents, such as tertiary amine, thioether, cyclic ether, can also be used; or both of the above two means can be applied to insure the formation of random block. Subsequently, residual 1~20wt% conjugated diene is added and transformed completely to form butadiene block.

Finally, coupling reagent is added to couple the polymer chains having active lithium end, thus, a star-shaped block copolymer is obtained.

The conjugated diene monomer of the present invention contains 4~6 carbon atoms, including 1,3-butadiene, isoprene, 2-ethyl-1,3-butadiene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, and mixture thereof, wherein 1,3-butadiene is preferred.

Monovinyl aromatic hydrocarbon monomer of the present invention contains 8~12 carbon atoms, including styrene, α -methyl styrene, β -ethenyl toluene, α -ethenyl toluene, β -ethenyl toluene, 4-ethyl styrene, and mixture thereof, wherein styrene is preferred.

In the present invention, polymerization process is performed in hydrocarbon solvent, in the suitable temperature range of 0~110℃, under the pressure of 2~4 Mpa, and the reaction mixture is substantially maintained in liquid phase. Exemplary hydrocarbon solvent includes straight chain alkane and cycloalkane, such as pentane, hexane, octane, cyclohexane and mixture thereof, wherein cyclohexane is preferred.

Small amount of polar compound, such as tetrahydrofuran, can be added into hydrocarbon solvent to increase the reaction activity of alkyl lithium, such as n-butyl lithium. At the same time, the polar compound can function as random reagent. The dosage of polar compound is 0.01~1.0 phm (portions of polar compound added into per 100 portions of monomer), the optimum range is 0.02~0.1 phm.

The initiator used in the invention is organolithium compound with a general formula of RLi , wherein R is C_4 ~ C_8 alkyl, cycloalkyl or aryl. The preferred initiators are n-butyl lithium and s-butyl lithium.

5 Polymerization reaction is performed under substantially oxygen-free and water-free conditions, preferred in inert atmosphere. After the reaction is finished, the system is treated by a method of adding CO₂ and water which is well-known in the art, to improve color and haze. Before evaporating the solvent, antioxidant is added, such as 2.6.4, 1010, TNP, 330 etc. They can be used independently or in combination.

10 Before processing into molded product or sheet material, this resin can be blended with various additives.

15 The resin produced in the present invention has high impact strength, and its elongation rate is greater than 200%, the polymerization period can be reduced by four times, and its transparency reaches the level of like products.

The product performances of the styrene-butadiene random block copolymer produced in the present invention are listed in Table 1.

15 Table 1 Main performances of styrene-butadiene random block copolymer resin

Performance sample	Tensile strength (Mpa)	Impact strength (Mpa)		Brinell hardness N/mm ²	Elongation rate %	Transparency %	Haze value %
		Ditch	No ditch				
ASTM	GB1040-79	GB1043-79		HG2-168-6 5	GB1040-7 9	-	-
Formula 1							
91-5-K-9	30.3	2.5	25.5	92.0	74	87.9	10.1
91-5-K-12	29.3	1.7	19.0	90.0	64	88.0	10.5
Formula 2							
91-6-K-2	24.7	3.6	20.3	76.0	136	88.6	9.5
91-6-K-3	24.6	3.2	15.7	78.0	120	88.7	8.5
Formula 3							
91-10-K-8	30.3	4.9	61.5	73.6	245	89.0	5.1
91-1-K-1	30.0	6.2	48.0	73.6	238	88.7	5.7
Formula 4							
90-5-K-9	29.0	4.8	33.0	93.0	130	84.7	13.6
90-5-K-11	23.0	4.2	22.0	92.0	142	85.7	8.0
Note						Transmissio n sheet □ 50 cm 2 cm thick	Transmissio n sheet □ 50 cm 2 cm thick

Examples

Polymerization reaction and coupling were carried out in a 14 L stainless reaction kettle; CO₂ and water were added into a 16 L stainless post-treating kettle to treat the colloid liquid. The sequence of feeding and the components are described as follows:

5 Step 1: 5500 g cyclohexane, 0.68 g tetrahydrofuran, and 1100 g styrene were added into the 14 L stainless reaction kettle respectively. After being stirred homogeneously, 2.13 g (0.033 mol) butyl lithium was added. Then the temperature was elevated to about 80°C, and the pressure was controlled to be 1~2 Mpa, and the time for polymerization was 30~50 minutes.

10 Step 2: 4450 g cyclohexane, 400 g styrene, and 490 g butadiene were added into a 5 L stainless batching kettle respectively. After being stirred homogeneously, the mixture was fed into the 14 L reaction kettle slowly. Then the temperature was elevated to about 80°C, and the pressure was controlled to be 2~4 Mpa, and the time for polymerization was 5~120 minutes.

15 Step 3: 20~100 g cyclohexane and 1~20 g butadiene were added into the 5 L stainless batching kettle respectively. After being stirred homogeneously, the mixture was fed into the 14 L stainless reaction kettle. Then the temperature was elevated to about 80°C, and the pressure was controlled to be 2~4 Mpa, and the time for polymerization was 30 minutes.

20 Step 4: Prepared coupling reagent [14 g cyclohexane, 1.66 g MeSi(OMe)₃] is fed into the 14 L stainless reaction kettle. Then the temperature was elevated to about 90°C, and the pressure was controlled to be 2~4 Mpa, and the time for coupling was 60~80 minutes.

25 Step 5: The colloid liquid was fed into the 16 L stainless post-treating kettle, then 60 g water and 0.15 m³ CO₂ were added. The reaction time was 10~20 minutes.

Step 6: An antioxidant (1~5wt% of dry colloid) was added into the 16 L post-treating kettle, and reacted for 10~20 minutes.



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[71]申请人 兰州化学工业公司化工研究院

地址 730060 甘肃省兰州市西固区合水路1号

[72]发明人 郭昌荣 刘昊 王兴亚

朱景芳 周志平

[74]专利代理机构 中国石油化工总公司兰州化学工业
公司专利事务所

代理人 杨光 王建明

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[54]发明名称 一种苯乙烯-丁二烯嵌段共聚物的制
备方法

[57]摘要

本发明涉及一种苯乙烯-丁二烯无规嵌段共聚物的制备方法,其步骤为在有机锂引发的苯乙烯-丁二烯阴离子聚合反应中,形成非弹性体嵌段之后生成无规化嵌段,最后形成弹性体的结构调节嵌段。这时,用烷氧基硅化合物偶合所形成的含活性端锂基聚合物链,使之生成星型结构的苯乙烯-丁二烯无规嵌段共聚物。

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权 利 要 求 书

1. 一种用三烷氧基硅烷类化合物作偶合剂制苯乙烯-丁二烯嵌段共聚物的方法，或者是用诸如环氧化聚丁二烯、环氧化大豆油、环氧化亚麻子油之类的多环氧化物，己二酸二酯类的多酯，四氯化硅之类的卤化物，1,2,4-三异氰酸酷苯类的多异氰酸酯、多胺、多元酮、多元碱、脱去二个水的苯均四甲酸之类的酸酐作偶合剂，制备通式为 $(S-S_1-B/S_2-B_1)_m-X-(B_1-B_2/S-S_1)_n$ 的无规嵌段共聚物；其特征在于采用三烷氧基硅烷类化合物作偶合剂，制备含有无规段的星型结构的苯乙烯-丁二烯嵌段共聚物。
2. 根据权利要求1所述的制备方法，其特征在于上述星型结构的无规嵌段共聚物可用式子 $(S-B'/S-B')_n-X$ 表示，其中，S代表聚乙烯基芳烃嵌段，B'代表聚共轭二烯烃嵌段，B'/S代表单乙烯基芳烃与共轭二烯烃的无规共聚物嵌段，n=3~4的整数，X代表偶合剂残基。
3. 根据权利要求1所述的制备方法，其特征在于单乙烯基芳烃为苯乙烯，共轭二烯烃为1,3-丁二烯，其引发剂为仲丁基锂。
4. 根据权利要求1所述的制备方法，其特征在于三烷氧基硅烷类化合物的结构为 $R-Si(OBu)_3$ ，其中R为1~12个碳的直链烷基、环烷基和芳香基。

说 明 书

一种苯乙烯-丁二烯嵌段共聚物的制备方法

本发明涉及一种用三烷氧基硅化合物 $RS_1(OR)_3$ 作偶合剂，使含有无规链段的活性聚合物偶合制备苯乙烯-丁二烯嵌段共聚物的方法。

现有生产技术中，报道苯乙烯-丁二烯嵌段共聚物的方法很多，其中一种是美国专利(3880954)所述，将苯乙烯和丁二烯共聚后，用甲基三甲氧基硅烷作偶合剂，使苯乙烯和丁二烯双嵌段的活性链偶合制备共聚物的方法；另一种是日本特许公报(昭63-92629)中报道的通式为 $(S-S_1-B/S_2-B_1)_m-X-(B_1-B_2/S-S_1)_n$ 的共聚物，其中X为多官能团基，m与n是等于X的官能度的整数($m < n$)，其值为3~20，S及 S_1 为乙烯基芳烃单体的聚合物嵌段， B_1 为最多占共聚物20%的共轭二烯烃的弹性体嵌段， B/S_2 及 B_2/S 为乙烯基芳烃化合物与共轭二烯烃的无规嵌段或乙烯基芳烃在乙烯基芳烃与共轭二烯烃共聚物中呈递减型嵌段。在这种方法中，所用的偶合剂为环氧化聚丁二烯、环氧化大豆油、环氧化亚麻子油之类的多环氧化物，己二酸二酯类的多酯，四氯化硅之类的卤化物，1,2,4-三异氰酸酯苯类的多异氰酸酯、多胺、多元酮、多元碱、脱去二个水的苯均四甲酸之类的酸酐。

采用上述方法制备的嵌段共聚物的冲击强度不很理想，当提高冲击强度高时，其综合性能却明显下降。

本发明的目的是提供一种使用三烷氧基硅烷类化合物作偶合剂，制备苯乙烯-丁二烯无规嵌段共聚物的方法，以改善树脂的冲击强度，提高树脂的透明度。

为了达到上述目的，本发明提供一种结构式为 $(S-B/S'-B')_n-X$ 的嵌段共聚物。其中S表示聚乙烯基芳烃嵌段， B/S' 表示乙烯基芳烃和共轭二烯烃的无规共聚物嵌段， B' 表示聚共轭二烯烃嵌段，n为3~4的整数，X代表偶合剂残基。

本发明的方法中，首先制成非弹性体(树脂性的)链段。在聚合釜中加入70~95%的乙烯基芳烃，使之与有机锂引发剂接触，搅拌20~60分钟，使所加乙烯基芳烃充分转化为具有活性锂原子端基的非弹性体链段。之后，在聚合釜中加入剩余的单

乙烯基芳烃和共轭二烯烃的混合物，其中共轭二烯烃占80~99%，在温度为0~110℃下反应5~120分钟，以形成单乙烯基芳烃和共轭二烯烃的无规共聚物嵌段。单体混合物可以连续地加入反应釜中（加料速度应低于反应速度），也可以使用无规化试剂，如三级胺、硫醚、环状醚；也可以既加入无规化试剂，又控制加料速度，从而保证生成无规化嵌段。之后，加入剩余的1~20%（重量）的共轭二烯烃，并使之转化完全，形成聚丁二烯嵌段。

最后加入偶合剂使生成的具有活性锂原子端基的聚合物链偶合，生成星型嵌段共聚物。

本发明中的共轭二烯烃单体含有4~6个碳原子，包括1,3-丁二烯、异戊二烯、2-乙基-1,3-丁二烯、2,3-二甲基-1,3-丁二烯和1,3-戊二烯以及它们的混合物，其中，最好使用1,3-丁二烯。

本发明中单乙烯基芳烃单体含有8~12个碳原子，包括苯乙烯、 α -甲基苯乙烯、对-乙烯基甲苯、间-乙烯基甲苯、邻-乙烯基甲苯、4-乙基苯乙烯以及它们的混合物，其中，最好使用苯乙烯。

本发明中，聚合过程在烃类溶剂中进行，适宜的温度范围为0~110℃，一般在2~4MPa压力下，使反应混合物基本上保持液相，较好的烃类溶剂包括直链烷烃和环烷烃，如戊烷、己烷、辛烷、环己烷和它们的混合物，其中最好的是环己烷。

可以向烃类溶剂中加入少量极性化合物，如四氢呋喃，以提高烷基锂，如正丁基锂的反应活性，同时它又是无规化试剂，其用量为0.01~1.0phm（每100份单体总量中添加的份数），最佳范围为0.02~0.1phm。

本发明中使用的引发剂通式为RLi的有机锂化合物，其中R是含有4~8个碳原子的烷基、环烷基或芳基。目前比较好的引发剂是正丁基锂和仲丁基锂。

聚合反应在基本上无氧和无水的条件下进行，最好在惰性气体环境中进行。反应完成后，该系统用技术上所熟知的加CO₂和水的方法处理，以改善颜色和雾度。在蒸出溶剂前，加入抗氧剂，如2、6、4，1010、TNP、330等均可，它们可以单用，也可以复合使用。

在加工制品如模制品和片材之前，该树脂可与各种添加剂掺混使用。

采用本发明制备的树脂，其冲击强度高且伸长大于200%，可缩短聚合周期4倍，透明度达到同类产品水平。

采用本发明制得的苯乙烯-丁二烯无规嵌段共聚物的产品性能见表1。

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